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BUREAU OF CHEMISTRY—BULLETIN No. 101.

H. W. WILEY, Chief of Bureau.

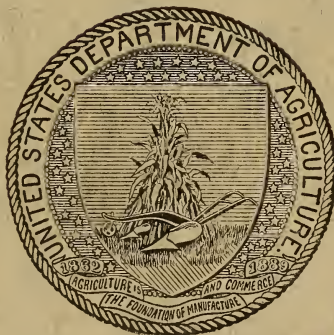
THE LIME-SULPHUR-SALT WASH AND ITS SUBSTITUTES.

BY

J. K. HAYWOOD,

CHIEF OF MISCELLANEOUS LABORATORY,

IN COLLABORATION WITH THE BUREAU OF ENTOMOLOGY.



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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF CHEMISTRY,

Washington, D. C., December 16, 1906.

SIR: I have the honor to transmit herewith a report on a number of practical studies made in this Bureau, in cooperation with the Bureau of Entomology, on the composition of certain insecticides concerning which there have been many inquiries received. I recommend that this manuscript be published as Bulletin No. 101 of the Bureau of Chemistry.

Respectfully,

H. W. WILEY,

Chief.

Hon. JAMES WILSON,

Secretary of Agriculture.

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THE LIME-SULPHUR-SALT WASH AND ITS SUBSTITUTES.

INTRODUCTION.

During the past two years the Miscellaneous Laboratory of the Bureau of Chemistry, at the request of the Bureau of Entomology, has made a number of studies of the composition and decomposition of the lime-sulphur-salt wash and its substitutes, and the results of these studies have appeared in various publications from time to time. Recently much more extended studies have been made, which, together with the earlier work, are presented in the present report. All of the experiments reported in this bulletin have a practical significance and were conducted with a view to solving certain problems arising in actual practice, questions concerning which are often asked by correspondents both of the Bureau of Entomology and the Bureau of Chemistry.

Messrs. B. H. Smith and Charles Goodrich, of the Bureau of Chemistry, assisted in the analytical work, and Messrs. C. L. Marlatt and A. L. Quaintance of the Bureau of Entomology, made many valuable suggestions in regard to the solution of the problems presented.

THE LIME-SULPHUR-SALT WASH.

EFFECT OF TIME OF BOILING ON COMPOSITION OF WASH.

The first experiment was to determine the composition of the lime-sulphur-salt wash, using constant amounts of the various ingredients but boiling for varying lengths of time, or, in other words, to study the effect of the time of boiling on the composition of the wash. For this purpose chemically pure reagents were employed, and a fractional part of the following formula used: Lime 30 pounds, sulphur 20 pounds, salt 15 pounds, and water 60 gallons, the boiling being carried on in a closed enamel boiler. After mixing the above ingredients, and before heating, the volume of the mixture was determined, and in every experiment thereafter, whatever the time of boiling and the consequent reduction in volume, the total volume was made up to the volume as first determined, and aliquot portions taken for analysis. Theoretically each 100 cc of such a mixture as the above should contain 5.55 grams of calcium oxid and 3.89 grams of sulphur, in case there had been no loss by volatilization or mechanically.

METHOD OF EXAMINING THE TOTAL WASH.

The mixture was boiled for the required length of time, made up to the correct volume as determined above, thoroughly shaken and 100 cc portions taken for analysis. This portion was weighed, poured through a weighed Gooch, well exhausted, and the residue dried at 110° C., and weighed. The difference between the total weight of 100 cc of the mixture and the weight of the residue was taken to be the weight of the liquid portion in 100 cc of the mixture. An aliquot portion of the liquid portion was weighed to obtain the weight of 1 cc. The total weight of the liquid divided by the weight of 1 cc gives the number of cubic centimeters of liquid in 100 cc of the whole mixture. The soluble sulphur and calcium oxid were next determined in 1 to 5 cc of the liquid. The results obtained on 1 cc of the liquid multiplied by the number of cubic centimeters of the liquid in 100 cc of the mixture give the weight of the dissolved sulphur and calcium oxid in 100 cc of the original wash. The residual and volatile sulphur reckoned together and the residual calcium oxid were obtained by subtracting the soluble sulphur and calcium oxid from the theoretical total amount of sulphur and calcium oxid, respectively. The method used for determining the soluble calcium oxid was the oxalate method usually employed, so it needs no explanation. The Avery method^a for determining soluble sulphur was used. The following results were obtained on five washes boiled for different lengths of time:

TABLE I.—*Lime and sulphur in 100 cc of the lime-sulphur-salt wash boiled for varying periods.*

Time of boiling. ^a	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium oxid.	Total calcium oxid.
Minutes.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
15	3.03	0.86	3.89	1.64	3.91	5.55
30	3.66	.23	3.89	1.95	3.60	5.55
45	3.72	.17	3.89	1.93	3.62	5.55
60	3.75	.14	3.89	2.13	3.42	5.55
90	3.45	.42	3.89	1.85	3.70	5.55

^a The mixture was brought to a boil before the time was taken.

From the above table it would appear (1) that the solid sulphur was not completely dissolved by 15 minutes' boiling; (2) that a 30-minute period of boiling was not quite long enough; (3) that a 45 to 60 minute period of boiling dissolved practically all of the sulphur present, and is consequently the best length of time to boil the wash to get a maximum amount of sulphur in solution. By continuing the boiling beyond one hour the mixture became very thick, with the quantity of materials used, and probably some of the sulphur was lost mechanically.

An attempt was next made to determine what compounds of sulphur are found in this wash, and whether they are changed by varying the

^a U. S. Dept. Agr., Bureau of Chemistry, Bul. 90, p. 105; Cir. 10, Rev., p. 10.

period of boiling. To do this the following methods of analysis were used:

METHOD OF EXAMINING THE LIQUID PORTION OF THE WASH.

Sulphur in solution as sulphids.—Pipette 25 cc of the liquid portion of the wash into a 100 cc flask and make up to the mark. Use 10 cc of this, representing 2.5 cc of the original solution, for analysis. Add an ammoniacal zinc chlorid solution (made by dissolving 3.253 grams of pure zinc in hydrochloric acid, supersaturating with ammonia, and making up to a liter) until slightly in excess, as shown by adding a drop of the solution to nickel sulphate. Place on the steam bath and heat until the odor of ammonia becomes faint, filter, and wash. Transfer filter and contents to a beaker, add about 10 to 15 cc of a saturated solution of potassium hydroxid, and heat for some time. Add 50 cc of hydrogen dioxid, free of sulphates, and heat on the steam bath exactly 30 minutes. Acidify with hydrochloric acid and precipitate with barium chlorid in the usual way.

Sulphur in solution as thiosulphates.—Pipette 5 cc of the original solution into a 50 cc flask and add ammoniacal zinc chlorid until it is slightly in excess, as shown by nickel sulphate. Make this mixture up to the mark, shake, and filter off through a dry filter. To a 25 cc aliquot of the filtrate add methyl orange and titrate with tenth-normal hydrochloric acid to exact neutrality. Next titrate the liquid with a tenth-normal iodine solution. The reading thus obtained gives the total thiosulphates and sulphites; since, however, the sulphites are present in such small amounts as to be negligible the number of cubic centimeters of iodine solution used may be considered to represent only the thiosulphates.

Sulphur as combined sulphates and sulphites.—Proceed as in the preceding method to the point where the thiosulphates have been changed to tetrathionates, and sulphites to sulphates by the addition of tenth-normal iodine. Make slightly acid with hydrochloric acid and precipitate the combined sulphates and sulphites (now sulphates) with barium chlorid in the usual way.^a

Working by these methods the following results were obtained on the liquid portion of the wash:

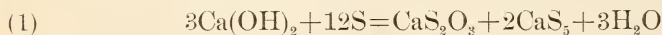
TABLE II.—*Sulphur compounds in 100 cc. of the liquid portion of the lime-sulphur-salt wash boiled for varying periods.*

Time of boiling.	Sulphur as thio-sulphates.	Sulphur as sulphids and poly-sulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
<i>Minutes.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
15	0.63	2.59	0.004	3.224
30	.76	2.91	.004	3.674
60	.84	2.91	.01	3.76
90	.86	2.92	.01	3.79

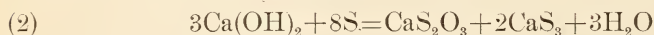
^a This method of analysis and those that follow are combinations of Avery's method for determining sulphur with certain methods given in Sutton's Volumetric Analysis, modified to meet the conditions here presented.

Three points are brought out by the above results: (1) A 1-hour period of boiling dissolves practically all of the sulphur; (2) the thiosulphates are somewhat increased by a more prolonged period of boiling; (3) the combined sulphates and sulphites are somewhat increased by a more prolonged period of boiling.

Reactions involved.—It is probable that the primary reaction in the combination of sulphur and lime which takes place is as follows:

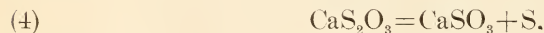


Such a reaction, however, would lead to the formation of less sulphur as thiosulphate and more sulphur as pentasulphid than is indicated in Table II. It is therefore probable that either one or both of the two following secondary reactions take place, both of which would lead to the formation of more thiosulphate and less polysulphid, thus approximating the figures in the table.

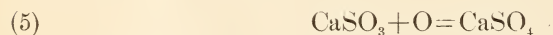


The sulphur set free in this last reaction would on further boiling combine with more lime to form thiosulphate and polysulphid. If the boiling be continued, it will be seen that more thiosulphate would constantly be formed at the expense of the pentasulphid. Since the figures given indicate that more thiosulphate and less polysulphid are formed than is indicated by the first theoretical equation, it is probable that equation (3) is the principal or only secondary reaction leading to the formation of thiosulphate.

It is well known that thiosulphates in solution change slowly to sulphites, which in turn change to sulphates, according to the following reactions:



and



It is therefore probable that sulphates and sulphites are found in the wash because of the above changes. The five reactions given are well known and can be found in any of the leading books of reference.^a As would be expected, therefore, there are found in the lime-sulphur-salt wash comparatively large quantities of pentasulphid and thiosulphate and extremely small quantities of sulphates and sulphites.

^a Mendeléeff's Principle of Chemistry; Thorpe's Dictionary of Applied Chemistry; Fremy's Chemical Encyclopædia, etc.

EFFECT OF SODIUM CHLORID ON THE COMPOSITION OF THE WASH.

An experiment was next carried out to determine whether or not the sodium chlorid used had any influence upon the amount and relative quantities of the various sulphur compounds in the wash. The same formula was used as in the first experiment, and a 1-hour period of boiling employed for both the wash with salt and the wash without salt. The following results were obtained:

TABLE III.—*Sulphur compounds in 100 cc of the liquid portion of the wash with and without salt.*

Composition of the wash.	Sulphur as thiosulphates.	Sulphur as sulphids and poly- sulphids.	Sulphur as sulphites and sul- phates.	Total sulphur.
	Grams.	Grams.	Grams.	Grams.
Lime-salt-sulphur	0.84	2.91	0.01	3.76
Lime-sulphur	.88	2.92		3.80

It is evident from these results that salt has practically no influence upon the composition of the wash in so far as the sulphur compounds are concerned, and therefore the following experiments were performed without the addition of salt.

EFFECT OF COMMERCIAL REAGENTS AND CHANGE OF FORMULA ON THE LIME-SULPHUR WASH.

To ascertain whether approximately the same time was required to get all sulphur in solution if high grade commercial reagents were employed instead of chemically pure ones, and also whether changing the formula from the one previously used to one commonly employed by orchardists had any influence upon the time necessary to get a maximum amount of sulphur in solution, another set of experiments was conducted. The formula used was as follows: Lime 20 pounds, sulphur 15 pounds, and water 50 gallons, good grades of commercial stone lime and sulphur being used. The results obtained are given in Tables IV and V.

TABLE IV.—*Lime and sulphur in 100 cc of lime-sulphur wash, using modified formula and commercial reagents.*

Time of boiling.	Sulphur in solution.	Residual and vola- tile sul- phur.	Total sul- phur.	Calcium oxid in so- lution.	Residual calcium oxid.	Total cal- cium oxid.
<i>Minutes.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
15	2.50	0.90	3.40	1.30	3.20	4.50
30	3.13	.27	3.40	1.69	2.81	4.50
45	3.19	.21	3.40	1.78	2.72	4.50
60	3.18	.22	3.40	1.88	2.62	4.50
120	3.19	.21	3.40	1.87	2.63	4.50

TABLE V.—*Sulphur compounds in 100 cc of the liquid portion of the lime-sulphur wash, using modified formula and commercial reagents.*

Time of boiling.	Sulphur as thio-sulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
<i>Minutes.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
15	0.48	2.05	0.02	2.55
30	.63	2.54	.02	3.19
45	.68	2.54	.02	3.24
60	.69	2.52	.02	3.23
120	.74	2.50	.02	3.26

From these results it is evident (1) that the solid sulphur was not completely dissolved by 15 minutes' boiling; (2) that a 30-minute period of boiling was not quite sufficient; (3) that a 45 to 60 minute period of boiling dissolved practically all the sulphur; (4) that the thiosulphates were somewhat increased by a more prolonged period of boiling. Since these are exactly the same as the conclusions reached in the first experiment, it is evident that a slight change in formula has no influence upon the time of boiling necessary to dissolve all the sulphur, nor has a substitution of high grade commercial lime and sulphur for the chemically pure articles any influence upon the same point.

LIME-SULPHUR WASHES PREPARED ACCORDING TO DIFFERENT FORMULAS.

The next set of experiments was to determine the composition of lime-sulphur mixtures boiled the same length of time (one hour), but containing varying quantities of lime and sulphur. Fractional parts of the following formulas were used in preparing the mixtures.

TABLE VI.—*Various formulas used in preparing experimental lime-sulphur washes.*

Number of experiment.	Sulphur.	Lime.	Water.
	<i>Pounds.</i>	<i>Pounds.</i>	<i>Gallons.</i>
1	25	30	50
2	25	20	50
3	15	25	50
4	15	20	50
5	15	15	50

The results obtained on the five different washes described in Table VI are given in Tables VII and VIII.

TABLE VII.—*Lime and sulphur in 100 cc of five lime-sulphur washes of varying composition.*

Number of experiment.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium oxid.	Total calcium oxid.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1	5.22	0.48	5.70	2.89	3.91	6.80
2	5.30	.40	5.70	2.76	1.74	4.50
3	3.20	.20	3.40	1.80	3.90	5.70
4	3.17	.23	3.40	1.76	2.74	4.50
5	3.17	.23	3.40	1.73	1.67	3.40

TABLE VIII.—*Sulphur compounds in 100 cc of the liquid portion of five lime-sulphur washes of varying composition.*

Number of experiment.	Sulphur as thio-sulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphites and sulphates.	Total sulphur.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1	1.08	4.26	0.02	5.36
2	.99	4.34	.02	5.35
3	.69	2.53	.01	3.23
4	.67	2.53	.01	3.21
5	.66	2.53	.01	3.20

From these results the following conclusions are drawn:

(1) The proportion of one part of lime to one of sulphur gives more than enough lime to dissolve the maximum amount of sulphur. (Experiment 5.)

(2) If more lime than the amount first mentioned is added in proportion to the sulphur it only remains present as so much excess lime and does not aid in the solution of more sulphur. (Experiments 3, 4, 5.)

(3) With a constant amount of sulphur present and varying amounts of lime, not only is the total sulphur practically constant but the various sulphur compounds present are the same. (Experiments 3, 4, 5.)

(4) Twenty-five pounds of sulphur per 50 gallons is about the maximum quantity, or a little more than the maximum quantity, that can be dissolved. This fact is shown, not only by the residual sulphur being present in considerable quantities in the two formulas where 25 pounds of sulphur were used (experiments 1 and 2), but also by the fact that in both of these cases when the wash cooled down to room temperature needles of an orange color, evidently a sulphur compound, crystallized out.

(5) It would also appear from experiment 2 that sufficient lime is present when it is used in the proportion of 1 part of lime to $1\frac{1}{2}$ parts of sulphur, but the experiment on this point is marred by the fact that in this formula as much or a little more sulphur is present than can go into solution in the amount of water used. According to the theoretical reaction one could use almost twice as much sulphur as lime and yet get all the sulphur in solution. It is extremely doubtful, however, whether the reaction would completely take place under these circumstances or whether, if it did so, it would not require an exceedingly long period of boiling. In addition to these considerations, in practice a moderate excess of lime is needed to exert its caustic action on the scale.

Taking all of these points into consideration it would appear, on purely theoretical grounds, that approximately the following formula should be used to obtain, at a minimum cost, a wash with the maximum amount of sulphur in solution and a moderate excess of lime, namely—water 50 gallons, lime 20 to 22.5 pounds, sulphur 22.5 pounds.

Whether or not this formula would give the best results in actual orchard practice is a subject for experimentation.

LIME-SULPHUR WASHES PREPARED WITH DIFFERENT KINDS OF LIME.

Experiments were next conducted to determine what effect the use of air-slaked lime instead of quicklime would have on the composition of a wash prepared according to one of the common formulas. For this purpose the formula, lime 20 pounds, sulphur 15 pounds, water 50 gallons, with a 1-hour period of boiling, was used. The air-slaked lime employed had not of course been left in the air a sufficient length of time to entirely change to carbonate but was merely the powder left after stone lime had fully slaked in the open air. The results obtained are given in Tables IX and X.

TABLE IX.—*Lime and sulphur in 100 cc of lime-sulphur wash, using air-slaked and quicklime.*

Kind of lime.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.
	Grams.	Grams.	Grams.	Grams.
Quicklime	3.18	0.22	3.40	1.88
Air-slaked	3.26	.14	3.40	1.62

TABLE X.—*Sulphur compounds in 100 cc of the liquid portion of lime-sulphur wash, using air-slaked and quicklime.*

Kind of lime.	Sulphur as thiosulphate.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
	Grams.	Grams.	Grams.	Grams.
Quicklime	0.69	2.52	0.02	3.23
Air-slaked	.68	2.60	.02	3.30

From these figures it is evident that the employment of moderately air-slaked lime has practically no influence on the composition of the wash. The sulphur compounds formed are nearly the same in amount as when quicklime is used, but the amount of lime in solution appears to be slightly larger when quicklime is employed. The writer is more inclined to ascribe this slight difference in the amount of dissolved lime to slight errors in the analysis than to any real difference. It is self-evident that if the air-slaked lime were left in the air long enough to become wholly changed to carbonate it could not be used to prepare the wash.

LIME-SULPHUR WASHES PREPARED WITH THE HEAT GENERATED BY QUICKLIME.

In this experiment, to determine whether a lime-sulphur wash could be prepared with no external heat, using only the heat generated by

slaking the lime, a constant amount of sulphur was used and varying amounts of lime. The wash so obtained was then compared with a wash prepared by the same formula, but boiled until the maximum amount of sulphur had dissolved. Following are the formulas used and the results obtained:

TABLE XI.—*Formulas used for preparing lime-sulphur washes.*

Number of experiment.	Lime.	Sulphur.	Water.	Time of heating.
	Pounds.	Pounds.	Gallons.	Hours.
1	40	15	50	0
2	30	15	50	0
3	30	15	50	1

TABLE XII.—*Lime and sulphur in 100 cc of lime-sulphur washes prepared by boiling and with the heat of slaking lime.*

Number of experiment.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium oxid.	Total calcium oxid.
	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
1	0.25	3.15	3.40	0.23	8.77	9.00
2	.19	3.21	3.40	.20	6.60	6.80
3 (Boiled)	3.16	.24	3.40	1.74	5.06	6.80

TABLE XIII.—*Sulphur compounds in 100 cc of the liquid portion of lime-sulphur washes prepared by boiling and with the heat of slaking lime.*

Number of experiment.	Sulphur as thiosulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
	Grams.	Grams.	Grams.	Grams.
1	0.04	0.21	0.02	0.27
2	.03	.15	.02	.20
3 (Boiled)	.71	2.50	.03	3.24

From these experiments it is evident that a satisfactory wash can not be made with the heat generated by slaking lime, not even if a large excess of lime is used so that a maximum amount of heat will be generated.

LIME-SULPHUR WASHES PREPARED WITH DIFFERENT FORMS OF SULPHUR.

In this experiment, to determine the effect of the form of sulphur used on the composition of the wash, the following formula was employed and the boiling continued for 1 hour: lime 20 pounds, sulphur 15 pounds, water 50 gallons. Three forms of sulphur were used, namely, flowers of sulphur, flour sulphur, and another form known in the South as crystallized sulphur. The last-named form of sulphur comes from Louisiana and is obtained from the ore by melting out the sulphur and allowing it to solidify as brimstone. It is then shipped

in lumps as it breaks under the pick. It presents smooth, hard, crystalline surfaces to view. The following results were obtained:

TABLE XIV.—*Lime and sulphur in 100 cc of lime-sulphur washes prepared with different forms of sulphur.*

Form of sulphur used.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium oxid.	Total calcium oxid.
	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
Flowers.....	3.17	0.23	3.40	1.76	2.74	4.50
Flour.....	3.30	.10	3.40	1.81	2.69	4.50
Crystalline.....	3.06	.34	3.40	1.51	2.99	4.50
	1.36	2.04	3.40	.70	3.80	4.50

TABLE XV.—*Sulphur compounds in 100 cc of the liquid portion of lime-sulphur washes prepared with different forms of sulphur.*

Form of sulphur used.	Sulphur as thiosulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
	Grams.	Grams.	Grams.	Grams.
Flowers.....	0.68	2.55	0.02	3.25
Flour.....	.68	2.67	.02	3.37
Crystalline.....	.58	2.53	.01	3.12
	.27	1.11	.01	1.39

It is evident from these analyses that there is practically no difference in the washes prepared with flowers of sulphur and flour sulphur, and that crystalline sulphur gives a wash of extremely variable composition, depending, no doubt, on the size of the particles of sulphur used and the time of boiling.

LIME-SULPHUR WASHES PREPARED WITH GROUND CRYSTALLINE SULPHUR.

Since the preceding experiment showed that the crystalline sulphur when used without powdering gave a wash of extremely variable composition, the following experiment was planned to determine what kind of a wash this form of sulphur would give if it were finely powdered, and how long it was necessary to boil the powdered crystalline sulphur to get all of the sulphur in solution.

The same formulas were used as described in the preceding experiment, but the sulphur was ground and boiled in the first experiment for $1\frac{1}{2}$ hours, and in the second for 2 hours. The following results were obtained:

TABLE XVI.—*Lime and sulphur in 100 cc of the lime-sulphur wash, using ground crystalline sulphur.*

Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium oxid.	Total calcium oxid.	Time of boiling.
Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Hours.
3.04	0.36	3.40	1.76	2.74	4.50	$1\frac{1}{2}$
3.13	.27	3.40	1.80	2.70	4.50	2

TABLE XVII.—*Sulphur compounds in 100 cc of the liquid portion of the lime-sulphur wash, using ground crystalline sulphur.*

Sulphur as thiosulphate.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.	Time of boiling.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Hours.</i>
0.65	2.44	0.01	3.10	1½
.70	2.48	.01	3.19	2

From these figures it is evident that even if the crystallized sulphur is ground to quite a fine powder it is in such a form that it dissolves more slowly than the flowers of sulphur or the flour sulphur. It also appears that with the ground crystalline sulphur about 2 hours' boiling is necessary to get the maximum amount of sulphur in solution. This increased time necessary to dissolve the crystalline sulphur is evidently due to its physical characteristics.

COLOR OF THE LIME-SULPHUR WASH.

Before leaving the consideration of the composition of the lime-sulphur-salt or the lime-sulphur wash, a word in regard to the correct color of the wash may be of value. The writer has seen many different statements in regard to this matter. Some claim that the wash when finally prepared should be yellow, some golden, some orange, some brown, and some olive green.

To test the color a wash was prepared with chemically pure lime and sulphur, boiling until all sulphur had dissolved. It was found that the color of the supernatant liquid was almost exactly the same as that of the skin of a dark, rusty-coated orange. When the mixture was stirred so that the white lime was evenly distributed throughout the solution, the color was much lighter. With most grades of commercial lime the colors of the supernatant liquid and of the total mixture were as just described; in the case of a few limes that came under the writer's observation, however, it was observed that the mixture when finally prepared was an olive green. On allowing the mixture to settle, the supernatant liquid was orange just as one would expect it to be, but the lime at the bottom was a deep olive green. It is therefore evident that the olive-green color of the mixture noted by some observers is due to impurities in the lime—probably compounds formed by the action of the sulphids of the wash on iron and manganese in the lime.

DECOMPOSITION OF THE LIME-SULPHUR-SALT WASH ON TREES.

An attempt was next made to determine what changes take place in the sulphur compounds of the wash when it is sprayed upon the tree. To imitate as closely as possible actual spraying conditions, measured

samples of the filtered wash, 5 cc usually, were absorbed by a large quantity of filter paper, which had been cut in slips and placed in large porcelain dishes. These dishes were immediately put in the open air in direct sunlight and the paper allowed to dry. This usually took about one hour. The dishes were then placed in a protected place in the open air and allowed to stand for varying lengths of time. In one series of experiments the paper was moistened each morning to simulate the effect of dew; in another series it was allowed to remain undisturbed until analyzed.

From the studies already made of the composition of the wash, the following changes would be expected when the paper was allowed to dry in the open air: (1) The pentasulphid would be oxidized to thiosulphate and sulphur according to the equation: $\text{CaS}_5 + \text{O}_3 = \text{CaS}_2\text{O}_3 + \text{S}_3$. This would result in the formation of more thiosulphate than was already present, and the deposition of free sulphur in a very finely divided form. (2) The total thiosulphate would then be changed to some extent to sulphite and deposit free sulphur, i. e.: $\text{CaS}_2\text{O}_3 = \text{CaSO}_3 + \text{S}$. (3) The sulphite would then be partially oxidized to sulphate according to the equation: $\text{CaSO}_3 + \text{O} = \text{CaSO}_4$. Finally, then, we would expect to find in the wash after it had dried on the tree, free sulphur, calcium thiosulphate, and small quantities of calcium sulphate and sulphite. The longer the action of the air and the dew continued, the less calcium thiosulphates we would expect to find present and the more sulphites and sulphates. Of course calcium hydroxid would be present, which would gradually be changed to calcium carbonate. Sodium chlorid, in case it were used, appears to have no influence on the composition of the wash and would very likely remain as such on the tree.

To experimentally prove or disprove the above assumptions, a wash was prepared by boiling the following constituents together for one hour: Lime 30 pounds, sulphur 20 pounds, and water 50 gallons. The composition of 100 cc of the liquid portion of this wash was found to be as follows:

	Grams per 100 cc.
Sulphur as thiosulphates.....	0.85
Sulphur as polysulphids and sulphids.....	2.93
Sulphur as sulphates and sulphites	.02
Total	3.80

METHODS OF EXAMINING THE DECOMPOSED WASH.

The following methods were used to determine the composition of the wash after drying on filter paper.

Total free sulphur.—Extract the filter paper in a Soxhlet extractor with redistilled carbon bisulphid, evaporate the carbon bisulphid, dissolve the residual sulphur in concentrated potassium hydroxid by boiling, and determine the sulphur as sulphate according to the Avery

method. Allow the filter paper remaining from the above treatment to stand till all the carbon bisulphid has evaporated, then beat it to a pulp with water and transfer the mass to a Gooch filter. Continue the extraction with water till the washings amount to about 450 cc of water, and determine the soluble sulphur compounds present in this filtrate. Repeat the washing with 450 cc of water several times, or until all the soluble sulphur compounds are extracted, and determine the sulphur compounds in the filtrates. Analyze the successive 450 portions of filtrate (sometimes amounting to three in number and even to six before all the soluble sulphur compounds are extracted) and add the results obtained, to get the total sulphur content in its variable soluble forms.

Sulphur as sulphids.—Remove a few drops of the first filtrate and test qualitatively for sulphids and polysulphids. (Neither were found in the experiments reported.) Then analyze each 450 cc filtrate by the following methods: Add methyl orange and titrate the solution tenth-normal hydrochloric acid to exact neutrality. Make up the volume to the 500 cc mark.

Sulphur as sulphates and sulphites.—Titrate a 250 cc portion of each of the above filtrates with iodine solution till the brown color of the iodine appears. Add a little more hydrochloric acid, boil the solution, precipitate with barium chlorid in the usual manner, and finally weigh as barium sulphate. (By this method the thiosulphate is changed to tetrathionate and the sulphite to sulphate, so that sulphates and sulphites are determined together as sulphates. The weak point in this determination is the fact that the tetrathionate seems to decompose to a *very slight extent* in boiling with hydrochloric acid, thus forming sulphate.)

Sulphur as sulphites and thiosulphates.—Measure off in a beaker a known volume of tenth-normal iodine (about 4 cc for the first filtrate and 0.2 to 0.3 cc for the subsequent filtrates), add water and as much of the 250 cc of the neutral filtrate left above titrated against the iodine as is necessary to arrive at the end point, using starch as indicator. This figure represents the sulphite and thiosulphate in a known volume of the 500 cc filtrate, and can be calculated back to the amount of iodine necessary for the whole filtrate. The solution was titrated against the iodine rather than the iodine against the solution, because it has been found by many investigators that more constant results are obtained in this way.

Sulphur as sulphites.—To the solution in a known quantity of which the sulphites and thiosulphates have been determined, as above, by means of tenth-normal iodine, add a little methyl orange and titrate to neutrality with tenth-normal sodium hydroxid. From this figure calculate the sulphite present in the whole 500 cc filtrate. This method of analysis is based on the following principle: When a thiosulphate is

changed to a tetrathionate by iodine, there is no change in the reaction of the solution, because both the thiosulphate and tetrathionate are neutral. When a bisulphite which is neutral to methyl orange is oxidized, however, by iodine to bisulphate, the solution becomes acid, both from the hydriodic acid set free and the bisulphate formed, and the combined quantity of these two, as determined by tenth-normal sodium hydroxide, is a measure of the sulphite present. In the above analysis all sulphites were changed to bisulphites by the original titration of the solution with tenth-normal hydrochloric acid to neutrality.^a

Sulphur as sulphates.—Subtract the sulphur as sulphites from the total sulphur as sulphates and sulphites.

Sulphur as thiosulphates.—Subtract from the total iodine figure obtained for thiosulphates and sulphites an amount of iodine corresponding to the sulphites as determined above and calculate the resulting iodine to thiosulphates.

Following are the results obtained on allowing four samples of the wash to stand in the open air for varying periods of time, after being absorbed by slips of filter paper.

TABLE XVIII.—*Composition of dry lime-sulphur-salt wash after standing.*

[Expressed in grams per 100 cc of solution.]

SAMPLES NOT WATERED.

Time of standing.	Free sulphur.	Sulphur as thiosulphates.	Sulphur as sulphites	Sulphur as sulphates.	Total sulphur.
(a) 5 days	1.71	1.97	0.11	0.01	3.80
(b) 5 days	1.72	1.97	.10	.01	3.80
(c) 8 days	1.74	1.94	.137	.01	3.83
(d) 8 days	1.77	1.94	.12	.02	3.85

SAMPLES WATERED TO SIMULATE DEW.

(e) 10 days	1.94	1.66	0.22		3.82
(f) 10 days	1.93	1.69	.20		3.82
(g) 4 weeks	2.11	1.42	.29	0.15	α 3.97
(h) 4 weeks	2.13	1.41	.27	.16	α 3.97

^aThe rather high results obtained for total sulphur in these two determinations is doubtless owing to errors in analysis, especially in the thiosulphate figures. The method of analysis outlined above is very difficult of execution, even under the best circumstances. In these two determinations six extractions of 500 cc each were necessary to extract all soluble sulphur compounds. This resulted in very small amounts of material being present in the last four 500 cc filtrates, and consequently the chances of error in the determinations were increased.

From Table XVIII it is evident that just those changes take place in the wash when it dries on the tree that the theoretical equations would lead one to expect. Analyses (a) and (b), after 5 days, indicate that the following reaction has taken place: $(1) \text{CaS}_5 + \text{O}_3 = \text{CaS}_2\text{O}_3 + 3\text{S}$, resulting in a deposition of sulphur and an increased formation of

^aA discussion of these methods of analysis is given on page 353 of the 8th edition of Sutton's Volumetric Analysis.

calcium thiosulphate. These two analyses also indicate that the following reaction has begun: $(2) \text{CaS}_2\text{O}_3 = \text{CaSO}_3 + \text{S}$, resulting in the formation of more calcium sulphite and more free sulphur.

Analyses (c) and (d), after 8 days, indicate that the reaction shown above as (2) has gone still further and that the following reaction has commenced— $(3) \text{CaSO}_3 + \text{O} = \text{CaSO}_4$ —resulting in the formation of more calcium sulphate. Analyses (e) and (f), after 10 days, indicate that the rapidity of reactions (2) and (3) has been much increased by wetting the paper every day or in practice by the wetting of the branches every day by the dew.

Analyses (g) and (h), after 4 weeks, indicate that the above reactions (2) and (3) have gone still further, resulting in the breaking up of about one-fourth of the thiosulphate and the consequent increase in free sulphur, sulphates, and sulphites. If the decomposition of the wash continued at the same rate as is indicated above, it would take it about four or five months to completely decompose, at least under these artificial conditions. When the decomposition of the thiosulphate was complete a very large amount of free sulphur would still be upon the tree; calcium sulphate and calcium sulphite would also be present. Still later the sulphite would be oxidized to sulphate, so that finally only free sulphur and calcium sulphate would be present, after perhaps four to six months. In case of a very hot sun shining upon the tree the sulphur itself might be volatilized, leaving only calcium sulphate.

THEORY OF THE ACTION OF THE WASH ON INSECTS.

From the above data a theory can be formed in regard to the action of this wash. First, consider a case in which the wash, after being sprayed upon the tree, remains practically untouched by rains for several months, as in the dry climate of California, so that the products of decomposition remain on the tree a long time. First, the excess of lime in the wash is quite caustic, and thus loosens the scales from the tree and exposes the insects. Almost at once the pentasulphid, on decomposing, deposits sulphur in a very finely divided condition, which has its usual insecticidal value, but just how this is exerted is not known. The thiosulphate present in the wash, together with that formed by the decomposition of the pentasulphid, probably has some insecticidal properties also. Next the thiosulphate begins to decompose and sets free sulphite and more free sulphur. This decomposition of the thiosulphate probably extends over several months. It is a well-known fact that sulphites act as antiseptic agents. There is reason to believe that they would also act as insecticides. From the decomposition of the wash there are obtained sulphur in a very finely divided form, thiosulphate for a time, and sulphite which is gradually set free. The writer is of the opinion that these are the

active agents in killing insects. This theory of the action of the wash would also explain why it continues to be efficacious over a considerable length of time.

In a wet climate, on the other hand, if a heavy rain should occur a day or two after the wash was applied, all the thiosulphate which was originally present, together with that which had been formed by the decomposition of the pentasulphid would probably be washed away. No sulphite could then be formed by slow decomposition of the thiosulphate. There would, therefore, be left upon the tree free sulphur as the only compound having insecticidal properties. The efficacy of the wash would, therefore, be much reduced. Again, if light rains occurred occasionally after the wash had been applied, its efficacy would be reduced just in proportion to the amount of thiosulphate and sulphite washed away.

It has been suggested by Mr. F. H. Pough, manager of the Bergen Port Sulphur Works of New York City, that the efficiency of the lime-sulphur-salt wash was due almost entirely to the finely divided sulphur set free on the decomposition of the pentasulphid. In support of this the widespread use of sulphur as a fungicide and insecticide was cited, more particularly its use for the prevention of the powdery mildew in vineyards, where it is often sprinkled on the hot ground to the windward of the plants, as well as on them; also to the value of sulphur dusting to destroy the red spider of citrus trees.

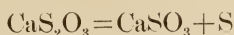
It is believed by Mr. Pough that the action of the wash is to be attributed to the gradual oxidation of sulphur which gives rise to sulphur dioxid, or sulphurous acid, where moisture is present, and that it is these constituents that do the work. In support of this theory he cites the cases where an odor resembling sulphur dioxid is plainly discernible on hot sunny days in the vicinity of orchards sprayed with the above mixture.

While the writer does believe that finely divided sulphur is one of the active insecticidal agents in the wash, though just how it acts is not known, he is inclined to doubt very much whether this oxidation of the sulphur alone would be rapid enough to be of great value. The following points are against this theory:

(1) If the action were at all considerable, it would be expected that the total sulphur on the tree would decrease, since not all the sulphur dioxid formed would be likely to be absorbed by the calcium hydroxid or calcium carbonate present, these being only mechanically mixed with the sulphur. In the "paper experiments," which to be sure are artificial, no loss of sulphur was shown after four weeks.

(2) It would be expected that the free sulphur would decrease during the course of four weeks by conversion to sulphur dioxid; instead of this, it increases to a slightly greater extent than corresponds to the

amount of sulphur formed from the breaking up of thiosulphate, according to the following equation:



(3) In regard to the odor resembling that of sulphur dioxid observed by Mr. Pough, those who have sublimed sulphur know that during sublimation this odor is very noticeable, so that the odor noticed in the vicinity of orchards on a hot sunny day may be due to subliming sulphur.

On the whole, while it is believed that some of the finely divided sulphur is oxidized, it seems doubtful whether enough is oxidized to make this factor a major one in determining the efficiency of the wash. It seems more probable that the combined action of all the sulphur compounds present, exclusive of the sulphate, gives to the wash its value.

THE LIME-SULPHUR-SALT-SODA WASH.

Having completed the study of the lime-sulphur-salt wash and the lime-sulphur wash prepared by various formulas and under different conditions, experiments were next undertaken along similar lines with the lime-sulphur-salt-soda and the lime-sulphur-soda washes. These washes have been suggested as substitutes for the older wash, without the soda, since it is said they can be prepared without any or with a minimum amount of boiling, thus saving the farmer much time and trouble.

LIME-SULPHUR-SALT-SODA WASH PREPARED WITHOUT EXTERNAL HEAT.

The first experiment was to determine the composition of a lime-sulphur-salt-soda wash prepared without external heat and compare it with that of a lime-sulphur-salt wash containing the same amounts of lime, sulphur, salt, and water, but boiled until the maximum amount of sulphur was dissolved. The following formulas and methods of procedure were followed, using chemically pure reagents:

For the lime-sulphur-salt-soda wash 30 pounds of lime, 20 pounds of sulphur, 15 pounds of salt, 10 pounds of caustic soda, and 60 gallons of water were used, and for the lime-sulphur-salt wash the same formula was employed exclusive of the caustic soda. The sulphur was made into a thin paste with 9 quarts of hot water, the lime slaked with 9 gallons of hot water, and the sulphur paste added to it. Then the caustic soda was stirred in and the mixture boiled of itself for a considerable period. Salt was then added and the requisite amount of water to make up 60 gallons plus the space occupied by the solids, as determined by previous tests in the experiments with the lime-sulphur-salt wash. The lime-sulphur-salt wash was prepared by

simply boiling the constituents together and making up to volume as in the previous experiments. The results given in Table XIX were obtained:

TABLE XIX.—*Lime and sulphur in 100 cc of the lime-sulphur-salt-soda wash.*^a

Constituents.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium oxid.	Total calcium oxid.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
Lime-sulphur-salt-soda	3.25	0.64	3.89	0.73	4.82	5.55
Lime-sulphur-salt.....	3.75	0.14	3.89	2.13	3.42	5.55

^a The various sulphur compounds present in this mixture were not determined.

It is evident from these data that all of the sulphur is not dissolved by the heat generated by the caustic soda, and, further, that the sulphur that does go into solution does so to a great extent as the sodium, instead of the calcium, salts of the sulphur acids, thus causing a smaller amount of calcium oxid to be dissolved and a larger amount to remain as a residue than in the case of the lime-sulphur-salt mixture.

LIME-SULPHUR-SALT-SODA WASH PREPARED BY HEATING FOR A SHORT PERIOD.

Since the preceding experiment showed that the method of preparation of the lime-sulphur-salt-soda wash, without the aid of heat, did not dissolve all the sulphur, another experiment was made to determine whether the maximum amount of sulphur would be dissolved by heating for a very short period. The following results were obtained using chemically pure reagents, the same formulas as in the preceding case, and a 20-minute period of heating, that being the time necessary to bring the mixture from room temperature up to the boiling point.

TABLE XX.—*Lime and sulphur in 100 cc of the wash prepared with 20 minutes' heating.*

Constituents.	Time of heating.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium.	Total calcium.
	<i>Minutes.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
Lime-sulphur-salt-soda ^a	20	3.79	0.10	3.89	0.75	4.80	5.55
Lime-sulphur-salt ^b	60	3.75	.14	3.89	2.13	3.42	5.55

TABLE XXI.—*Sulphur compounds in 100 cc of the liquid portion of the wash prepared with 20 minutes' heating.*

Constituents.	Sulphur as thiosulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
Lime-sulphur-salt-soda ^a	0.88	3.04	0.005	3.925
Lime-salt-sulphur ^b	.84	2.91	.010	3.760

^a Twenty minutes to bring to boil.

^b Sixty minutes' boiling.

The following facts are indicated by Tables XX and XXI: (1) Practically all of the sulphur goes into solution in the lime-sulphur-salt-soda wash when it is heated for 20 minutes. (2) This treatment seems to dissolve a little more sulphur than by boiling with lime and salt for one hour. (3) The liquid portion of the lime-sulphur-salt-soda wash prepared as above contains the same sulphur acids in nearly the same amounts as the lime-sulphur-salt mixture, the only difference being that the sulphur compounds are present to a large extent as the sodium, instead of the calcium, salts. (4) More residual calcium oxid is present in the lime-sulphur-salt-soda wash than in the lime-sulphur-salt wash. (5) The former wash should be more caustic than the latter, both on account of the caustic soda present and also because of the greater excess of lime.

LIME-SULPHUR-SODA WASHES PREPARED WITHOUT EXTERNAL HEAT
AND BY ADDING CONSTITUENTS IN DIFFERENT ORDERS.

The next experiment was for the purpose of determining how much sulphur goes into solution when high grade *commercial* sulphur, stone lime, and caustic soda are used instead of the chemically pure articles, and what influence the order in which these ingredients are added has on the composition of the wash. For this purpose a wash was first prepared according to the following formula: Lime, 30 pounds; sulphur, 15 pounds; water, 50 gallons, boiling for one hour and using high grade commercial ingredients. This wash was used as the standard and another wash was prepared, using the same amount of ingredients with the addition of 6 pounds of caustic soda to generate the heat and form a good medium for dissolving the sulphur. The following procedure was followed in the preparation of the second wash: The sulphur was made into a thin paste with hot water and added to the slaking lime. When the lime had ceased to slake, the full amount of caustic soda was added and the mixture stirred for 15 minutes. Water was then added to make up to 50 gallons plus the space occupied by the solid reagents. This wash is designated as experiment 2.

In another sample of wash the same formula was used, but the order in which the ingredients were added was different, i. e., the sulphur was made in the form of a thin paste with hot water and the total caustic soda then added. The mixture was stirred for 15 minutes and the lime added and allowed to slake; water was then added to make up to 50 gallons plus the space occupied by the solid reagents. The mixture so made is designated as experiment 3.

The following results were obtained with these three washes:

TABLE XXII.—*Lime and sulphur in 100 cc of washes differently prepared.*

Number of experiment.	Ingredients.	Sulphur in solution.	Residual and volatile sulphur.	Total sulphur.	Calcium oxid in solution.	Residual calcium.	Total calcium.
		<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1	Lime-sulphur.....	3.16	0.24	3.40	1.74	5.06	6.80
2	Lime-sulphur-soda.....	2.27	1.13	3.40	.24	6.56	6.80
3	Sulphur-soda-lime.....	2.80	.60	3.40	.43	6.37	6.80

TABLE XXIII.—*Sulphur compounds in 100 cc of the liquid portions of washes differently prepared.*

Number of experiment.	Sulphur as thiosulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1	0.71	2.50	0.63	3.24
2	.41	1.91	.02	2.34
3	.47	2.37	.02	2.86

From these tables it is evident that high grade commercial samples of lime, sulphur, and soda, when used to prepare the lime-sulphur-soda wash, act practically the same as the chemically pure articles, resulting in the formation of a mixture containing about the same relative quantities of soluble sulphur compounds, though the amounts are decidedly smaller than those dissolved by boiling. Further, a better wash, i. e., one containing more sulphur in solution, is obtained by adding the ingredients in the order—sulphur, caustic soda, lime—than by mixing in the following order—lime, sulphur, caustic soda.

COMPARISON OF THE LIME-SULPHUR-SODA AND THE SULPHUR-SODA WASHES PREPARED WITHOUT EXTERNAL HEAT.

A comparison was next made of the composition of two washes, the first of which was prepared according to the following formula: Lime 30 pounds, sulphur 15 pounds, water 50 gallons, caustic soda 6 pounds, adding the constituents in the order—sulphur, caustic soda, lime—just as described in the preceding experiment. The second of the washes was prepared in the same way and by the same formula except that no lime was used. To make the comparison it was only necessary to examine the liquid portions of the washes. The following results were obtained, using high grade commercial ingredients:

TABLE XXIV.—*Sulphur compounds in 100 cc of the liquid portion of two washes prepared without external heat.*

Ingredients.	Sulphur as thiosulphates.	Sulphur as sulphids and polysulphids.	Sulphur as sulphates and sulphites.	Total sulphur.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
Lime-sulphur-soda.....	0.47	2.37	0.02	2.86
Sulphur-soda.....	.35	1.59	.03	1.97

From this study it will be seen that more sulphur goes in solution in the lime-sulphur-soda wash prepared as above than when the same amounts of sulphur and soda are used, but no lime; also that the sulphur-soda wash contains the same sulphur acids as the lime-sulphur-salt and the lime-sulphur-soda mixtures, the only difference being that a smaller amount of the sulphur is dissolved than in either of the above-named washes, and that the sulphur acids are present only as sodium salts instead of wholly or partially as calcium salts.

DECOMPOSITION OF THE LIME-SULPHUR-SALT-SODA WASH ON TREES.

A study was next made of the decomposition of the lime-sulphur-salt-soda wash along the same lines that were followed for the lime-sulphur-salt wash. For this purpose a wash of the following formula was used: Lime 30 pounds, sulphur 20 pounds, salt 15 pounds, caustic soda 10 pounds, and water 60 gallons. The mixture was heated 20 minutes to dissolve all of the sulphur. When finally prepared the sulphur compounds in the liquid portion of the wash were found to be as follows, chemically pure reagents being used:

	Grams per 100 cc.
Sulphur as thiosulphates.....	0.88
Sulphur as polysulphids and sulphids.....	3.04
Sulphur as sulphates and sulphites.....	.005
Total sulphur	3.925

Portions of this wash were dried on filter paper, as already described under the decomposition of the lime-sulphur-salt wash, and analyses of the same were made from time to time, with the following results:

TABLE XXV.—*Composition of the lime-sulphur-salt-soda wash after drying*

[Expressed in grams per 100 cc of solution.]

Time of standing.	Free sulphur.	Sulphur as thiosul- phates.	Sulphur as sulphites.	Sulphur as sulphates.	Total sulphur.
<i>Days.</i>					
9 ^a	1.57	2.27	0.02	0.00	3.86
28 ^a	1.64	2.14	.06	.02	3.86
12 ^b	1.64	2.19	.04	.01	3.88
27 ^b	1.74	1.88	.10	.02	3.74

^a Not watered to represent dew.

^b Watered to represent dew.

From these data it is evident that the lime-sulphur-salt-soda wash decomposes in the same manner as the lime-sulphur-salt wash except that the rate of decomposition is much slower. Such being the case, it would appear, on purely chemical grounds, that the wash with caustic soda added ought to give just as good results as the original lime-sulphur-salt wash, if prepared so as to contain a like amount of sulphur. In fact, better results might be expected, since the sodium hydroxid is more caustic than the lime and would therefore tend to

loosen the scale better, so that the other ingredients of the wash could act more thoroughly. However, two points must be taken into consideration: (1) That sodium sulphite, which is slowly formed, is more soluble than calcium sulphite, so that in a damp climate it would be washed off more easily; (2) that the rate of decomposition of the lime-sulphur-salt-soda wash is slower than that of the lime-sulphur-salt wash, and therefore it is possible that such decomposition might not take place rapidly enough to make it as efficacious as the old wash, assuming, of course, that the products formed by the gradual and slow decomposition have insecticidal properties. In expressing the above opinions the writer does so purely on the analytical data obtained in these studies, and of course recognizes that field experiments are necessary to establish the truth or falsity of these conjectures.

PROPOSED NEW WASHES.

In the lime-sulphur-salt-soda wash the author is unable to see that anything is gained by the addition of salt, although it is recognized that some hold strenuously to the belief that the wash without it is a failure. Besides this it would appear that the caustic soda entirely takes the place of the lime, in so far as the caustic action of the wash on the scale is concerned. This is especially true in a dry climate where the caustic soda, which is much more soluble than the calcium hydroxid, is not washed off of the tree by rains. Therefore a wash composed only of sulphur, caustic soda, and water seems worthy of trial in combating scale insects. Such a wash should, of course, have approximately the same sulphur strength as the old lime-sulphur-salt wash and should require absolutely no heating to get the sulphur into solution. After a number of trials of different relative proportions of caustic soda, sulphur, and water it was found that if the formula as given below be used a mixture will be formed having in solution approximately the same amount of sulphur and the same sulphur compounds as the original lime-sulphur-salt wash, with the exception that these sulphur compounds exist entirely as the sodium salts instead of being present chiefly as calcium salts.

Proposed Formula.^a

Water.....	gallons..	50
Powdered sulphur.....	pounds..	19
Caustic soda.....	pounds..	10

The wash is mixed as follows: Make a paste of the sulphur with not more than $5\frac{1}{2}$ gallons of boiling water: at once add all the caustic soda, which has previously been broken up into pieces the size of a hickory

^a A wash somewhat similar to this has long been employed as a remedy for mites (sulphur 20 pounds, caustic soda, 98 per cent, 10 pounds, variously diluted), but not made according to the following directions nor with any understanding of its close chemical relationship to the lime-sulphur-salt wash.

nut or smaller, and stir occasionally for one-half hour. At the end of this time add $44\frac{1}{2}$ gallons of water, stir, and the wash is ready for use.

An analysis of the liquid portion of this wash for sulphur compounds shows the following composition:

	Grams per 100 cc.
Sulphur as thiosulphates.....	0.63
Sulphur as polysulphids and sulphids.....	2.85
Sulphur as sulphates and sulphites	.01
Total sulphur	3.49

It will be noted that this wash contains somewhat less sulphur than the original lime-sulphur-salt wash (formula—lime, 30 pounds; sulphur, 20 pounds; salt, 15 pounds; water, 60 gallons), but not enough to have any material influence. However, if others are of the opinion that it should be of exactly the same strength it can easily be made so by adding $39\frac{1}{2}$ gallons of water instead of $44\frac{1}{2}$ gallons of water, as given in the formula.

Again, it may be the opinion of many, and the opinion may prove to be correct, that it is best to add lime to this mixture, both on account of the fact that it serves as a guide in spraying and because it is less soluble in rain than caustic soda, and so will remain on the tree longer. If such is found to be the case the above formula could be used with the addition of about $17\frac{1}{2}$ pounds of slaked lime. The directions for preparing this wash would then read:

Make a paste of the sulphur with about $5\frac{1}{2}$ gallons of boiling water and add at once all the caustic soda, which has been previously broken up into pieces the size of a hickory nut or smaller, and stir occasionally for one-half hour, slake the lime with enough water to make a thick paste, and add the slaked lime to the mixture of sulphur, soda, and water. Add an amount of water equivalent to 50 gallons, minus the quantity already used in slaking the lime and making a paste of the sulphur.

Such a mixture as this is made in much the same way as one of the lime-sulphur-soda washes already described (p. 25), but different amounts of the ingredients are used and a slightly different procedure followed, which results in the solution of more sulphur and in the opinion of the writer produces a much better wash. It is believed, *on purely theoretical grounds and without having made field experiments*, that the first mixture proposed above, without lime, will give good results, especially in a dry climate. If this formula is deemed worthy of trial, reports as to its efficiency and the results obtained, as compared with those given by the lime-sulphur-salt wash, would be received with interest by the writer.

